

## Transient Nuclear-Magnetic-Resonance Study of the Conduction Band of Metallic $\text{Na}_x\text{WO}_3$ : $^{183}\text{W}$ Relaxation\*

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Transient nuclear-magnetic-resonance measurements reported previously for the  $^{23}\text{Na}$  resonance in metallic sodium tungsten bronzes  $\text{Na}_x\text{WO}_3$  have been extended to the  $^{183}\text{W}$  resonance in these compounds. Measurements of the  $^{183}\text{W}$  spin-lattice relaxation time  $T_1$  and the spin-echo phase-memory time  $T_2$  have been carried out for  $x=0.56, 0.65, 0.73, 0.81, \text{ and } 0.89$  in the temperature range  $1 \leq T \leq 4^\circ\text{K}$ . Whereas  $T_1T$  is at least  $4400 \text{ sec } ^\circ\text{K}$  for the  $^{23}\text{Na}$  resonance,  $T_1T$  was found to have values between 6 and  $16 \text{ sec } ^\circ\text{K}$  (depending on the  $x$  value) for the  $^{183}\text{W}$  resonance. An analysis of these relaxation times provides conclusive evidence that the conduction band in these compounds has no significant sodium  $3s$  or  $3p$  character, but instead is based on tungsten  $5d$  states as postulated initially by Sienko. Tungsten  $6s$  states play a relatively minor role in the conduction band, contributing less than 10% to the total density of states  $N(\epsilon_0)$  at the Fermi surface. Core polarization provides the largest contribution to the  $^{183}\text{W}$  resonance shift, whereas the orbital hyperfine interaction probably provides the most important of the conduction-electron contributions to nuclear relaxation. The orbital magnetic susceptibility in  $\text{Na}_x\text{WO}_3$  is estimated to be small, having an upper limit of  $10 \times 10^{-6} \text{ emu/mole}$  for  $x=0.56$  and  $18 \times 10^{-6} \text{ emu/mole}$  for  $x=0.89$ . These results should be contrasted with tungsten metal, for which the orbital susceptibility is large ( $\geq 66 \times 10^{-6} \text{ emu/mole}$ ); the orbital mechanism predominates in the resonance shift, and the  $s$ -contact mechanism provides the major conduction-electron contribution to nuclear spin-lattice relaxation.

### I. INTRODUCTION

At least four models<sup>1-5</sup> have been proposed in the literature to explain electronic conduction in the series<sup>6</sup> of metals  $\text{Na}_x\text{WO}_3$  ( $0.3 \lesssim x \lesssim 1.0$ ). These compounds have a cubic perovskite structure in which the tungsten atom lies in the center of the unit cell, the oxygen atoms lie in the face centers, and the sodium atoms are distributed over the corner positions. The crystal structure of metallic  $\text{Na}_x\text{WO}_3$  is thus related to that of  $\text{WO}_3$  (itself an insulator), with sodium atoms occupying interstitial positions. The models for the conduction band of  $\text{Na}_x\text{WO}_3$  can be classified according to the atomic states which form the basis for a tight-binding description. Briefly, these models are:

1. Sienko<sup>1,2</sup> model—tungsten  $5d(t_{2g})$  states.
2. Keller<sup>3</sup> model—tungsten  $6s$  states, with minimum energy when the wave vector is at a zone corner.
3. Mackintosh<sup>4</sup> model—sodium  $3p$  states.
4. Fuchs<sup>5</sup> model—probably restricted to sodium states by the assumption that conduction occurs only through lattice sites occupied by sodium atoms (i.e., the effective volume for conduction is  $x$ -dependent).

Nuclear magnetic resonance (NMR) has thus far proved to be the most effective probe into the electronic properties of these metallic compounds. Knight-shift

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<sup>1</sup> M. J. Sienko, *J. Am. Chem. Soc.* **81**, 5556 (1959).

<sup>2</sup> M. J. Sienko, *Nonstoichiometric Compounds*, edited by Robert F. Gould (American Chemical Society, Washington, D. C., 1963), Vol. 39, p. 224.

<sup>3</sup> J. M. Keller, *J. Chem. Phys.* **33**, 232 (1960).

<sup>4</sup> A. R. Mackintosh, *J. Chem. Phys.* **38**, 1991 (1963).

<sup>5</sup> R. Fuchs, *J. Chem. Phys.* **42**, 3781 (1965).

<sup>6</sup> H. R. Shanks, P. H. Sidles, and G. C. Danielson, *Nonstoichiometric Compounds*, edited by Robert F. Gould (American Chemical Society, Washington, D. C., 1963), Vol. 39, p. 237.

measurements of the  $^{23}\text{Na}$  resonance<sup>7</sup> and the  $^{183}\text{W}$  resonance<sup>8</sup> have yielded the initially unexpected results that the  $^{23}\text{Na}$  shift is extremely small and negative, while the  $^{183}\text{W}$  shift is larger but still negative. This contrasts with the large positive shifts observed for sodium<sup>9</sup> and tungsten<sup>10</sup> metals. The negative shifts in  $\text{Na}_x\text{WO}_3$  gave strong indication that  $s$  states are not very important in the conduction band. The Keller model therefore had to be abandoned, and Mackintosh was forced to restrict his formulation to the atomic  $p$  states of sodium, despite the fact that the conduction band in sodium metal has a great deal of  $s$  character.

Measurements of the nuclear spin-lattice relaxation rate are especially well-suited for a study of electronic conduction bands, particularly in metallic compounds containing more than one cationic constituent. This follows from the short-range character of the dominant hyperfine interactions. Our measurements<sup>11</sup> of the  $^{23}\text{Na}$  relaxation rate yielded the result that the conduction electrons are coupled very weakly to the  $^{23}\text{Na}$  nuclei. A comparison of the observed rates with calculations based on orbital and spin-dipolar hyperfine interactions established a conservative upper limit estimate of 33% for the admixture of sodium  $3p$  states in the conduction band, which in our opinion represents sufficient grounds in itself for discarding the Mackintosh and Fuchs models.

Recently our experimental technique for transient measurements was improved to a degree that enabled us to study the  $^{183}\text{W}$  resonance in W metal.<sup>10</sup> It was

<sup>7</sup> W. H. Jones, Jr., E. A. Garbaty, and R. G. Barnes, *J. Chem. Phys.* **36**, 494 (1962).

<sup>8</sup> A. Narath and D. C. Wallace, *Phys. Rev.* **127**, 724 (1962).

<sup>9</sup> W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 93.

<sup>10</sup> A. Narath and A. T. Fromhold, Jr., *Phys. Rev.* **139**, A794 (1965).

<sup>11</sup> A. T. Fromhold, Jr., and A. Narath, *Phys. Rev.* **136**, A487 (1964).

TABLE I. Spin-echo dephasing times ( $T_2^*$ ) and phase memory times ( $T_2$ ) for  $^{183}\text{W}$  in metallic  $\text{Na}_x\text{WO}_3$ .

$x$ value	$T_2^*$ (msec)	$T_2$ (msec)
0.89	0.090( $\pm 10\%$ )	23( $\pm 5\%$ )
0.81	0.090	23
0.73	0.090	27
0.65	0.075	28
0.56	0.050	35

therefore of interest to us to measure also the relaxation rate of the  $^{183}\text{W}$  resonance in  $\text{Na}_x\text{WO}_3$ , in order that a comparison between the  $^{23}\text{Na}$  and  $^{183}\text{W}$  rates could be made. In this paper we report results of an investigation of  $^{183}\text{W}$  spin relaxation rates in  $\text{Na}_x\text{WO}_3$  ( $x=0.56, 0.65, 0.73, 0.81,$  and  $0.89$ ) in the temperature range  $1-4^\circ\text{K}$ . The results of this study provide additional support for the Sienko model and thus corroborate our previous conclusions. Section II summarizes our experimental techniques. The experimental spin-spin relaxation rates are discussed in Sec. III. The experimental spin-lattice relaxation rates are presented and analyzed in Sec. IV. Conclusions are offered in Sec. V.

## II. EXPERIMENTAL DETAILS

The measurements reported in this paper were performed on the same samples which were used in our earlier studies.<sup>8,11</sup> These samples consisted of 325-mesh powders suspended in paraffin which were prepared several years ago.<sup>8</sup> The possibility that a significant sodium loss might have occurred by gradual diffusion across the bronze-paraffin interfaces was eliminated by repeating our  $^{183}\text{W}$  spin-relaxation measurements on a freshly crushed  $x=0.89$  specimen. Identical results were obtained as for the original  $x=0.89$  sample.

The relaxation times were determined by standard crossed-coil transient-induction techniques. Because of the small nuclear moment of  $^{183}\text{W}$  and its low natural abundance (14%) all experiments were carried out in a 55-kOe compensated superconducting solenoid. Temperatures in the range  $1-4^\circ\text{K}$  were attained by controlled pumping on liquid helium contained in a separate sample Dewar. Radiofrequency excitation was provided by an incoherent pulsed oscillator operating near 10 MHz. The  $^{183}\text{W}$  resonances were found to be broadened inhomogeneously and all measurements were therefore based on observations of the spin echo<sup>12</sup> following two equal-width rf pulses. Phase memory times  $T_2$  were determined by measuring the echo intensity as a function of time separation between the two rf pulses; spin-lattice relaxation times  $T_1$  were determined from the recovery of the echo amplitude following saturation of the nuclear magnetization by an rf "comb." The receiver was similar to that used previously.<sup>13</sup> In general, the observed transient signals

were considerably weaker than in the case of tungsten metal because of the lower density of the tungsten bronzes. For this reason the echo and calibration<sup>13</sup> signals were recorded by a Varian C-1024 time-averaging computer. Adequate signal-to-noise ratios were achieved by averaging over 25 or more repetitive time sweeps.

## III. SPIN-SPIN RELAXATION

The spin-echo dephasing times  $T_2^*$  (i.e., half-width of the echo between  $1/e$  points) and the phase memory times  $T_2$  were determined at several temperatures in the range  $1-4^\circ\text{K}$ . The results are independent of temperature and are listed in Table I.

The  $^{183}\text{W}$  nuclear resonances in our  $\text{Na}_x\text{WO}_3$  samples are characterized by strong inhomogeneous broadening as evidenced by the observation of very narrow spin echos ( $T_2^*=50$  to  $90 \mu\text{sec}$ ). The dephasing times correspond to linewidths in the frequency domain which vary from about 0.01 MHz for  $x=0.56$  to 0.005 MHz for  $x=0.89$ . These widths are at least an order of magnitude greater than those expected from the known magnetic field inhomogeneity of our magnet, but are consistent with the previous<sup>8</sup> cw observations. Since  $I=\frac{1}{2}$  for  $^{183}\text{W}$ , nuclear electric quadrupole interactions cannot be responsible for the line broadening. It is probable, therefore, that the linewidths are due to local variations of the chemical or Knight shifts resulting from the disordered arrangement of sodium atoms. It is noteworthy that the broadening has a magnitude which is nearly comparable to the Knight shift.<sup>8</sup> This suggests that the probability distribution of electrons in the vicinity of the tungsten atom depends in a significant way on the number of surrounding sodium atoms. The observed  $x$  dependence of  $T_2^*$  is in qualitative agreement with this argument since the number of nonequivalent sodium configurations which occur with high probability should be greatest in our  $x=0.56$  sample. For some reason not presently understood, the inhomogeneities responsible for the short  $T_2^*$  produced no observable distribution in the corresponding spin-lattice relaxation rates, as evidenced by the observation of recovery curves following saturation which were exponential. This suggests that the interactions which contribute significantly to the spin-lattice relaxation are different from those which are responsible for the small values of  $T_2^*$ .

Although our previous  $^{23}\text{Na}$  relaxation measurements<sup>11</sup> gave evidence for clustering of sodium atoms, the present measurements provide no additional information about this possibility. The reason for this is the absence of quadrupolar broadening in the  $^{183}\text{W}$  resonance ( $I=\frac{1}{2}$ ), whereas quadrupolar effects produced two clearly distinguishable signals for the  $^{23}\text{Na}$  resonance ( $I=\frac{3}{2}$ ) which were assigned to ordered and disordered regions of the sample.

The echo phase-memory decay curves for the  $^{183}\text{W}$  resonance have Gaussian shapes with characteristic

<sup>12</sup> E. L. Hahn, Phys. Rev. **80**, 580 (1950).

<sup>13</sup> A. Narath and D. W. Alderman, Phys. Rev. **143**, 328 (1966).

phase memory times ( $T_2=23$  to 35 msec) which are much longer than the dephasing times  $T_2^*$ . The major  $T_2$  mechanism must arise from the dipolar interaction with  $^{23}\text{Na}$  spins, since dipolar and indirect exchange interactions between tungsten nuclei can probably be neglected because of the small magnetic moment and low relative abundance (14.3%) of  $^{183}\text{W}$ . The dipolar interaction with  $^{23}\text{Na}$  spins yields a calculated second moment  $\langle\Delta H^2\rangle=0.30$  Oe<sup>2</sup> for  $x=1$ , corresponding to a  $T_2^*$  for the *free induction* decay of 2.2 msec. The phase memory time  $T_2$  should be much longer since it is determined entirely by the *fluctuations* in the local field. It is not possible, however, for us to explain in detail the origin of the long phase memory times  $T_2$  which we have observed experimentally.

The phase memory times discussed above for the  $^{183}\text{W}$  resonance should be compared with the corresponding values of  $T_2=0.2$  to 1.4 msec observed<sup>11</sup> for the  $^{23}\text{Na}$  resonance in these compounds. The difference in  $T_2$  for the two resonances is qualitatively as expected, since the dipolar interaction between sodium spins is stronger than that between tungsten and sodium spins.

#### IV. SPIN-LATTICE RELAXATION

The measured values of  $T_1T$  are listed in Table II. These values are independent of temperature in the range 1–4°K within an estimated experimental uncertainty of  $\pm 5\%$ . Signal-to-noise considerations limited accurate measurements to the first  $\sim 90\%$  of the magnetization recovery. In this interval the recovery curves were always exponential.

The observed spin-lattice relaxation rates (Table II) are more than two orders of magnitude faster than the corresponding conduction-electron rates for  $^{23}\text{Na}$  ( $T_1T \approx 4400$  sec°K)<sup>11</sup> in the same compounds, and also exceed the rate observed in tungsten metal ( $T_1T=37$  sec°K).<sup>10</sup> It is apparent, therefore, that the conduction electrons provide a spin-lattice relaxation mechanism for tungsten nuclei in  $\text{Na}_x\text{WO}_3$  which is as effective as the conduction-electron mechanism in ordinary metals, whereas these same conduction electrons provide an extremely ineffective spin-lattice relaxation mechanism for the sodium nuclei in  $\text{Na}_x\text{WO}_3$ . The immediate significance of this observation<sup>14</sup> is that tungsten states in a tight-binding description must contribute significantly to conduction-band states near the Fermi level in  $\text{Na}_x\text{WO}_3$ .

The product  $K^2T_1T$  can be computed, using the  $^{183}\text{W}$  Knight-shift values  $K$  listed in Table II which were published by Narath and Wallace<sup>3</sup> for  $\text{Na}_x\text{WO}_3$ . The combination of room-temperature Knight shifts with low-temperature relaxation rates should be valid since the magnetic susceptibility in cubic  $\text{Na}_x\text{WO}_3$  is temperature-independent<sup>15</sup> below room temperature.

<sup>14</sup> A. T. Fromhold, Jr., and A. Narath, *Bull. Am. Phys. Soc.* **10**, 606 (1965).

<sup>15</sup> J. D. Greiner, H. R. Shanks, and D. C. Wallace, *J. Chem. Phys.* **36**, 772 (1962).

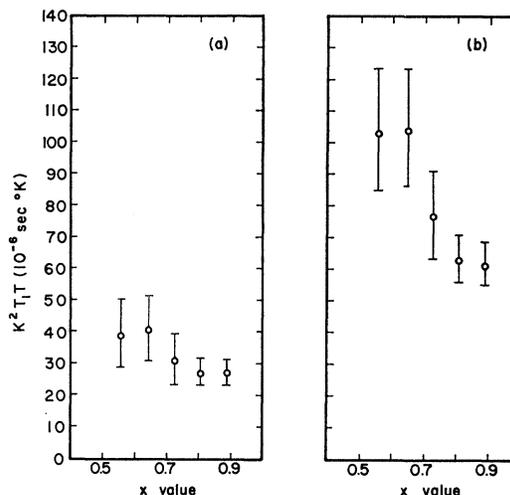


FIG. 1. Experimental values of  $K^2T_1T$  versus  $x$  value computed from the Knight shift and nuclear spin-lattice relaxation rate for the  $^{183}\text{W}$  resonance in  $\text{Na}_x\text{WO}_3$ . Reference compounds: (a)  $\text{WF}_6$ ; (b)  $\text{WO}_3$ .

Knight shifts relative to two reference compounds are given in Table II because the chemical shifts are of appreciable magnitude. Use of the electrical insulator  $\text{WO}_3$  as a reference compound is appealing because of its structural relationship to  $\text{Na}_x\text{WO}_3$ , although there remains the question of the diamagnetic contribution of the sodium cores to the chemical shift which might cause in addition a small  $x$ -dependent shift of the resonance frequency. The subsequent analysis yields conclusions which are essentially invariant with respect to the choice of reference compound, so this point will not be further discussed. Plots of the experimental product  $K^2T_1T$  versus the  $x$  value for both reference compounds are given in Fig. 1. The values of  $K^2T_1T$  are of the order of  $3 \times 10^{-5}$  sec°K using  $\text{WF}_6$  as the reference compound and of the order of  $8 \times 10^{-5}$  sec°K using  $\text{WO}_3$  as the reference compound.

The experimental values of  $K^2T_1T$  may be compared with the value predicted by the well-known Korringa relation<sup>16,17</sup>

$$K^2T_1T = \frac{\hbar}{4\pi k_B} \left( \frac{\gamma_e}{\gamma_n} \right)^2, \quad (1)$$

where  $\gamma_e$  and  $\gamma_n$  are the electronic and nuclear gyromagnetic ratios, respectively,  $2\pi\hbar$  is Planck's constant, and  $k_B$  is the Boltzmann constant. This relation, which is based on the assumption that the electronic states at the Fermi surface have 100%  $s$  character, yields  $K^2T_1T=15 \times 10^{-5}$  sec°K for  $^{183}\text{W}$ . The fact that the experimental  $T_1T$  is a factor of 2 to 5 smaller than predicted from the measured Knight shift by the Korringa relation indicates cancellation of a nonzero positive resonance shift given by the sum of  $s$ -contact<sup>9</sup> and

<sup>16</sup> J. Korringa, *Physica* **16**, 601 (1950).

<sup>17</sup> C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963), p. 126.

TABLE II. Nuclear spin-lattice relaxation ( $T_1T$ ) and Knight-shift ( $K$ ) data<sup>a</sup> for  $^{183}\text{W}$  in metallic  $\text{Na}_x\text{WO}_3$ .

$x$ value	$T_1T$ (sec $^\circ\text{K}$ )	$10^3K$ ( $\text{WF}_6$ reference)	$10^3K$ ( $\text{WO}_3$ reference)
0.89	6.8( $\pm 5\%$ )	$-2.01 \pm 0.09$	$-3.01$
0.81	7.3	$-1.94 \pm 0.10$	$-2.94$
0.73	10.0	$-1.76 \pm 0.18$	$-2.76$
0.65	13.6	$-1.76 \pm 0.18$	$-2.76$
0.56	15.3	$-1.59 \pm 0.18$	$-2.59$

<sup>a</sup> Knight-shift data from Ref. 8.

orbital mechanisms<sup>18</sup> by a negative shift due to the core-polarization<sup>19,20</sup> mechanism. The conclusion that the core-polarization contribution to the resonance shift is predominant follows immediately from the fact that the total shift is negative.<sup>8</sup>

It has been suggested<sup>4</sup> that the measured  $^{183}\text{W}$  shifts in  $\text{Na}_x\text{WO}_3$  might represent chemical shifts. The observation of very rapid conduction-electron-induced spin-lattice relaxation rates for  $^{183}\text{W}$  shows that this is not the case. Instead, the tungsten resonance experiments show quite clearly that tungsten  $d$  states play a dominant role in the conduction-band of the sodium tungsten bronzes.

Apart from the above qualitative but nevertheless definitive conclusions resulting from our measurements, some quantitative analysis can be performed. The values of  $\chi_s$  and  $\chi_d$ , the spin contributions of the  $s$  and  $d$  functions comprising the conduction band, can be estimated from the independent-electron relations<sup>21</sup>

$$\begin{aligned}\chi_s &= 2\mu_B^2 N_s(\zeta_0), \\ \chi_d &= 2\mu_B^2 N_d(\zeta_0),\end{aligned}\quad (2)$$

where  $\mu_B$  is the Bohr magneton. The respective state densities  $N_s(\zeta_0)$  and  $N_d(\zeta_0)$ , for one direction of the spin, are those at the Fermi level  $\zeta_0$ . The total density of states

$$N(\zeta_0) = N_s(\zeta_0) + N_d(\zeta_0), \quad (3)$$

can be obtained from the low-temperature specific-heat coefficient  $\gamma_{el}$  using the independent-electron relation

$$N(\zeta_0) = \frac{3}{2} \gamma_{el} (\pi k_B)^{-2}. \quad (4)$$

The electronic specific-heat coefficient  $\gamma_{el}$  measured by Vest *et al.*,<sup>22</sup> for the same samples as those used in the present measurements, and the state densities as well as spin susceptibilities deduced therefrom are listed in Table III.

Equations (1) and (3) of Ref. 10 (concerned with tungsten metal) are also applicable to the relaxation

<sup>18</sup> A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962).

<sup>19</sup> V. Heine, Phys. Rev. **107**, 1002 (1957).

<sup>20</sup> A. M. Clogston and V. Jaccarino, Phys. Rev. **121**, 1357 (1961).

<sup>21</sup> N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958), p. 185.

<sup>22</sup> R. W. Vest, M. Griffel, and J. F. Smith, J. Chem. Phys. **28**, 293 (1958).

TABLE III. Experimental values of the electronic specific-heat coefficient  $\gamma_{el}$ , and computed values for the total density of electronic states  $N(\zeta_0)$  at the Fermi surface (for one direction of the spin) and the total spin susceptibility  $\chi_s + \chi_d$ .

$x$ value	$\gamma_{el}$ (mJ/mole deg $^2$ ) <sup>a</sup>	$N(\zeta_0)$ ( $10^{11}$ cgs/atom)	$\chi_s + \chi_d$ ( $10^{-6}$ emu/mole)
0.89	$2.82 \pm 0.03$	3.74	38.7
0.81	$2.56 \pm 0.03$	3.39	35.1
0.73	$2.05 \pm 0.02$	2.71	28.1
0.65	$1.92 \pm 0.02$	2.54	26.3
0.56	$1.76 \pm 0.02$	2.33	24.1

<sup>a</sup> See Ref. 22.

rates and Knight shifts for the  $^{183}\text{W}$  resonance in  $\text{Na}_x\text{WO}_3$ . An estimate (based on Knight<sup>9</sup>) of  $3.85 \times 10^6$  Oe/electron for the  $s$ -contact hyperfine field  $H_{hf}(s)$  in tungsten metal was used in Ref. 10, and the approximate ratio 10: -1.0: 1.5 were deduced for  $H_{hf}(s): H_{hf}(d): H_{hf}(\text{orb})$ , where  $H_{hf}(d)$  and  $H_{hf}(\text{orb})$  are the core-polarization ( $d$ -spin) and orbital hyperfine fields, respectively. The least reliable of these estimates is that of  $H_{hf}(d) = -0.38$  kOe per electron since it was based on an assumed ratio  $H_{hf}(s): H_{hf}(d) = -10$ . Although this relationship is reasonably well obeyed by a number of transition metals for which independent determinations of  $H_{hf}(d)$  have been possible,<sup>23</sup> there is no firm theoretical basis for believing in its general validity. Among  $5d$  metals, core-polarization fields have been measured experimentally for Pt metal<sup>23</sup> [ $H_{hf}(d) = -1.18 \times 10^6$  Oe] and for La in  $\text{LaRu}_2$ <sup>24</sup> [ $H_{hf}(d) = -0.41 \times 10^6$  Oe], by relating temperature variations of the Knight shift to those of the magnetic susceptibility. A comparison of these values with our estimate for tungsten suggests that a somewhat larger core-polarization field would be more appropriate for tungsten.

In the present analysis, the  $s$ -contact and orbital hyperfine fields are also considered to be somewhat larger than those chosen for tungsten metal, since the relative degree of ionization<sup>9</sup> of the tungsten atom in partially ionic  $\text{WO}_3$  should be considerably greater than in tungsten metal. Furthermore, the relative degree of ionization could depend on  $x$  value, but this effect will be neglected. For convenience we have chosen to scale  $H_{hf}(s)$  used for tungsten metal by the factor  $\eta$ , while arbitrarily holding the ratios 10: -1.0: 1.5 fixed for the relative values of the three hyperfine fields. The parameter  $\eta$  is found to have values in the range 1.5-3.0, which is about what one would expect from estimates<sup>9</sup> given in the literature. It also yields a core-polarization field which is more consistent with the  $5d$  hyperfine field in Pt metal. The essential results of the analysis are not changed significantly if  $H_{hf}(d)$  is kept constant and the scale factor  $\eta$  only applied to  $H_{hf}(s)$  and  $H_{hf}(\text{orb})$ .

<sup>23</sup> A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. **134**, A650 (1964).

<sup>24</sup> D. Shaltiel, A. C. Gossard, and J. H. Wernick, Phys. Rev. **137**, A1027 (1965).

With the above substitutions, Eq. (1) of Ref. 10 yields the following expressions for the  $s$ -contact,<sup>15</sup> core-polarization,<sup>25</sup> and orbital<sup>26</sup> relaxation rates [ $R_i = (T_1 T)^{-1}$ ], respectively, in units of  $(\text{sec}^\circ\text{K})^{-1}$ :

$$R_s = 335 \times 10^{-25} \rho^2 (\rho + 1)^{-2} \eta^2 N(\zeta_0)^2, \quad (5)$$

$$R_{\text{ep}} = 3.35 \times 10^{-25} (\rho + 1)^{-2} q \eta^2 N(\zeta_0)^2, \quad (6)$$

$$R_{\text{orb}} = 7.54 \times 10^{-25} (\rho + 1)^{-2} p \eta^2 N(\zeta_0)^2, \quad (7)$$

where

$$\rho = N_s(\zeta_0) / N_d(\zeta_0), \quad (8)$$

$$q = \frac{1}{3} f^2 + \frac{1}{2} (1 - f)^2, \quad (9)$$

$$p = \frac{2}{3} f (2 - (5/3) f), \quad (10)$$

with  $f$  denoting the average fractional admixture of  $5d(t_{2g})$  states at the Fermi surface. Adding the three rates together yields the total rate:

$$R = 3.35 \times 10^{-25} (\rho + 1)^{-2} \eta^2 N(\zeta_0)^2 \times [100\rho^2 + q + 2.25p]. \quad (11)$$

Similarly, Eq. (3) of Ref. 10 and the corresponding hyperfine field values yield the following expressions for the  $s$ -contact, core-polarization, and orbital shifts.

$$K_s = 7.10 \times 10^{-14} \rho (\rho + 1)^{-1} \eta N(\zeta_0), \quad (12)$$

$$K_{\text{ep}} = -0.710 \times 10^{-14} (\rho + 1)^{-1} \eta N(\zeta_0), \quad (13)$$

$$K_{\text{orb}} / K_{\text{ep}} = -1.5 \chi_{VV} / \chi_d, \quad (14)$$

where  $\chi_{VV}$  is the orbital magnetic susceptibility. Adding the three shifts together gives the total Knight shift  $K$ ,

$$K = 0.710 \times 10^{-14} (\rho + 1)^{-1} \eta N(\zeta_0) \times [10\rho - 1.0 + 1.5(\chi_{VV} / \chi_d)]. \quad (15)$$

Immediately we can conclude that  $10\rho + 1.5(\chi_{VV} / \chi_d)$  must be less than unity, since all the experimental shifts given in Table II are negative. Thus the admixture of  $s$  states in the conduction band is quite small, being less than 0.1 even in the limit of a zero  $\chi_{VV}$ . Furthermore, it can be concluded that  $\chi_{VV} < 0.7\chi_d$ .

The product  $K^2 T_1 T$  can now be formulated, using Eqs. (11) and (15), in units of  $(\text{sec}^\circ\text{K})$ :

$$K^2 T_1 T = 1.50 \times 10^{-4} \left[ \frac{\{10\rho - 1.0 + 1.5(\chi_{VV} / \chi_d)\}^2}{100\rho^2 + q + 2.5p} \right]. \quad (16)$$

This equation is independent of  $\eta$  but not of  $N(\zeta_0)$  (unless  $\chi_{VV} = 0$ ), since  $\chi_d$  depends on  $N(\zeta_0)$  according to Eqs. (2) and (3). It is clear from Eq. (16) that the  $x$  dependence of the product  $K^2 T_1 T$ , as illustrated in Fig. 1, could possibly be due to an  $x$  dependence of  $\rho$ ,  $f$ , or  $\chi_{VV} / \chi_d$ .

The use of Eq. (16) is limited, since  $\rho$  is unknown and the ratio  $\chi_{VV} / \chi_d$  is unknown. As an example of the type of analysis which can be carried out, we assume that  $\rho = 0$  (consistent with  $\rho < 0.1$  deduced above), but that  $\chi_{VV} \neq 0$ . The assumption that  $\rho = 0$  is equiva-

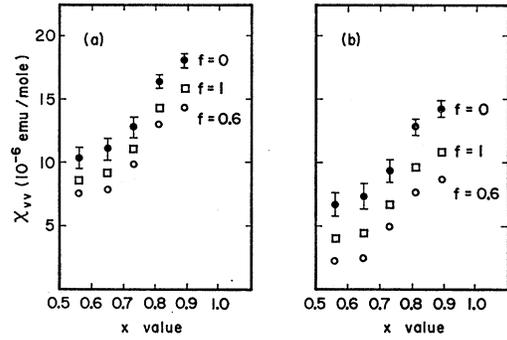


Fig. 2. Computed values for  $\chi_{VV}$  versus  $x$  value for three  $f$  values assuming a conduction band with 100%  $d$  character. Reference compounds: (a)  $\text{WF}_6$ ; (b)  $\text{WO}_3$ . (The error bars for  $f=0$  are determined by the experimental uncertainty in  $K^2 T_1 T$  for the reference compound in question.)

lent to the assumption that the conduction band has a negligible amount of tungsten  $6s$  character. Equation (16) then yields values for  $\chi_{VV} / \chi_d$  upon substitution of the measured values of  $K$  and  $T_1 T$  listed in Table II. The values depend of course on the reference compound and the choice of  $f$ , but the general conclusions are independent of both, as shown in the plots of  $\chi_{VV}$  versus  $x$  given in Fig. 2. Note that  $\chi_{VV}$  increases with  $x$  value, as expected for the filling of a nearly empty conduction band, and the deduced values do not depend significantly on the choice of the parameter  $f$ . The range for  $\chi_{VV}$  is  $7 \times 10^{-6}$  to  $18 \times 10^{-6}$  emu/mole based on the reference compound  $\text{WF}_6$ , or  $2 \times 10^{-6}$  to  $14 \times 10^{-6}$  emu/mole based on the reference compound  $\text{WO}_3$ . These values may be somewhat too large in view of the experimentally measured values<sup>15</sup> for the total susceptibility ( $\chi = \frac{2}{3}\chi_s + \chi_d + \chi_{VV} + \chi_{\text{dia}}$  increases from  $2 \times 10^{-6}$  to approximately  $14 \times 10^{-6}$  emu/mole as  $x$  increases from 0.5 to 0.9); closed-shell diamagnetic contributions  $\chi_{\text{dia}}$  of  $-24 \times 10^{-6}$  to  $-43 \times 10^{-6}$  emu/mole would therefore be necessary. This is not a serious flaw in the analysis, however, since an  $s$ -band contribution to  $N(\zeta_0)$  of 1 to 6% ( $0.01 \leq \rho \leq 0.06$ ) reduces  $\chi_{VV}$  sufficiently to give a reasonable fit to  $\chi$  for all  $x$  values using either the value of  $\chi_{\text{dia}} = -20 \times 10^{-6}$  emu/mole estimated by Greiner *et al.*,<sup>15</sup> or  $\chi_{\text{dia}} = -27 \times 10^{-6}$  emu/mole obtained from the magnetic measurements of Sienko and Banerjee.<sup>27</sup> Thus, the choice of  $\rho = 0$  gives an upper limit on  $\chi_{VV}$ . Quantitative agreement in such an analysis cannot be expected, of course, because of the unknown contributions of electron-electron and electron-phonon interactions to the magnetic susceptibility and electronic specific heat. The effective number of  $s$  electrons ( $n_s$ ) per tungsten atom which correspond to a given value of  $\rho$  may be estimated from the free-electron expression

$$n_s = (0.171 \times 10^{-30}) V^{-2} [N(\zeta_0) \rho / (\rho + 1)]^3, \quad (17)$$

<sup>25</sup> Y. Yafet and V. Jaccarino, Phys. Rev. 133, A1630 (1964).

<sup>26</sup> Y. Obata, J. Phys. Soc. Japan 18, 1020 (1963).

<sup>27</sup> M. J. Sienko and B. Banerjee, J. Am. Chem. Soc. 83, 4149 (1961).

where  $V$  is the molar volume in  $\text{cm}^3$ . For  $x=0.89$  and  $\rho=0.1$  we find  $n_s=0.0056$ .

The values of  $\eta$  can be deduced from Eq. (11) or from Eq. (15). Values consistent with the above analysis are typically 1.8, 2.1, and 2.6 for  $f$  values of 0.6, 1.0, and 0.0, respectively;  $\eta$  is independent of the reference compound for  $\rho=0$ . The value  $\eta=2.6$  is probably too large, since  $f=0.0$  would not be expected. In its simplest form Sienko's model,<sup>1,2</sup> for example, predicts that  $f=1.0$ . The value  $f=\frac{2}{3}$  corresponds to an equal contribution from all  $d$  orbitals to states near the Fermi level. No significant trend of  $\eta$  with  $x$  value could be detected.

No further conclusions are warranted by the above analysis because of uncertainties in many of the relevant parameters. They include the Knight shifts (owing to the unknown magnitude of chemical shifts), the  $f$  values, the ratio of the three hyperfine fields, as well as the variation of these quantities with  $x$  value. In addition, Eqs. (6) and (7) may not be entirely correct, even within the tight-binding approximation, because of the removal of cubic symmetry at the tungsten sites due to nonstoichiometry with respect to the sodium atoms. Finally possible deviations from the independent-electron model as a result of electron-phonon and electron-electron interactions have been ignored. A partitioning of the shifts and rates as was done for tungsten metal would be of great interest, but in the present case such a partitioning is not unique. In general, the results of a partitioning indicate the predominance of the orbital mechanism for relaxation. (Since our estimate of the core-polarization hyperfine field is not very reliable the ratio  $R_{\text{op}}/R_{\text{orb}}$  cannot, however, be determined very accurately.) The negative resonance shift, of course, indicates the predominance of core polarization for the shift. These results may be compared with those for tungsten metal where the contact interaction is the principal contribution to the spin-lattice relaxation ( $T_1^{183}\text{T}=37 \text{ sec}^\circ\text{K}$ ), and the orbital interaction accounts for the major part of the Knight shift ( $K^{183}=+0.0106$ ).

## V. CONCLUSIONS

The tungsten Knight shifts and spin-lattice relaxation rates in the cubic sodium tungsten bronzes  $\text{Na}_x\text{WO}_3$  provide convincing evidence for a high, predominantly  $d$ -like conduction-electron density at the tungsten lattice sites. The strong  $d$  character of states near the Fermi level leads to fast relaxation rates  $R^{183}$  and negative Knight shifts  $K^{183}$  as a result of the orbital and core-polarization mechanisms, respectively. The absence of large *positive* contributions to  $K^{183}$  shows that the static  $s$  contact and orbital interactions are relatively weak. Thus, the density of tungsten  $s$  states in the conduction band near the Fermi level is small (less than 10% of the total density of states). Furthermore, the orbital magnetic susceptibility is small as would be expected for a nearly empty  $d$  band whose

energy width is not much smaller than that observed in elemental transition metals such as tungsten.

The strong conduction-electron-induced hyperfine interactions observed for the tungsten nucleus should be contrasted with the long spin-lattice relaxation times<sup>11</sup> and small Knight shifts<sup>7</sup> observed for the sodium nucleus in  $\text{Na}_x\text{WO}_3$ . For example, the conduction-electron contribution to the  $^{23}\text{Na}$  spin-lattice relaxation<sup>11</sup> is  $T_1^{23}\text{T}=4.4\times 10^3 \text{ sec}^\circ\text{K}$  for  $x=0.73$ . The corresponding resonance shift<sup>7</sup> is  $K^{23}=-6\times 10^{-5}$  which, despite its small magnitude, appears to be too large for a  $\text{Na}^+$  chemical shift. In view of the negative sign of  $K^{23}$  it appears reasonable to attribute the conduction-electron-induced relaxation rates and shifts of the  $^{23}\text{Na}$  resonance to core-polarization processes. This interpretation is also supported by the fact that the product  $K^2T_1T$  has the magnitude expected for a core-polarization process.

There are two possible origins for the core-polarization process for sodium ions in these compounds. One possibility is that the exchange polarization of the sodium-core electrons is due to a partial sodium  $3p$  character of the conduction electrons. A second possibility<sup>11</sup> is that the  $3p$  admixture is zero but overlap between tungsten  $5d$  orbitals and sodium-core  $s$  orbitals produces a negative exchange polarization which yields the required hyperfine field at the sodium nucleus. In this case, the  $\langle r^{-3} \rangle$ -dependent contributions to  $R^{23}$  would be small. We believe the first possibility to be unlikely from the following argument. Goodings<sup>28</sup> has concluded on the basis of unrestricted Hartree-Fock calculations that the core-polarization contribution to the hfs of the sodium  $^2P$  term is positive and has a magnitude which is only 3% of  $\langle r^{-3} \rangle$ . However, it has been estimated<sup>11</sup> that a 33% admixture of sodium  $3p$  states at the Fermi level would be required to account for the observed values of  $R^{23}$  if relaxation is due entirely to orbital and spin-dipolar interactions. It is therefore concluded that a  $3p$  admixture cannot account for the negative  $^{23}\text{Na}$  resonance shifts. The second possibility (exchange polarization due to overlap between tungsten  $5d$  orbitals and sodium-core  $s$  orbitals), on the other hand, appears to be quite reasonable. The magnitude of the required core-polarization field can be estimated from the measured shifts together with the spin susceptibilities computed from the electronic specific heat. For  $x=0.73$ , we obtain  $H_{\text{hf}}(d)^{23}=-12 \text{ kOe/electron}$  as the total contribution from the eight tungstens which are nearest neighbors to the sodium atom.

Although the  $^{183}\text{W}$  relaxation rates and negative Knight shifts increase markedly with  $x$  value, as expected from the  $x$  dependence of the electronic specific-heat coefficient, the corresponding values<sup>7</sup> for  $^{23}\text{Na}$  are essentially independent of  $x$  value, with the exception of an anomalous  $K^{23}$  for the  $x=0.89$  sample. This lack of a definite  $x$  dependence for  $R^{23}$  and  $K^{23}$  still

<sup>28</sup> D. A. Goodings, Phys. Rev. **123**, 1706 (1961).

cannot be explained,<sup>11</sup> although the  $x$  dependence of the lattice parameter<sup>29</sup> ( $d \ln a_0/dx=0.021$ ) may be a contributing factor.

From the foregoing discussion it follows that the density of sodium states in the conduction band near the Fermi level is probably negligibly small. The sodium atoms therefore form  $\text{Na}^+$  ions in the  $\text{Na}_x\text{WO}_3$  structure, donating their valence electrons to the  $5d$  conduction band. The  $\text{Na}^+$  ions probably increase the effective overlap between the tungsten wave functions because of a decrease in the electrostatic potential near the edges of the unit cell. If this effect is important it follows that the conduction-band width should increase with increasing sodium concentration. A rigid band description of the dependence of the electrical properties on  $x$  value may therefore not be valid.

In summary, the present study, together with previous NMR measurements, provides strong support for

<sup>29</sup> B. W. Brown and E. Banks, *J. Am. Chem. Soc.* **76**, 963 (1954).

the Sienko<sup>1,2</sup>  $5d$  conduction-band model for the sodium tungsten bronzes. In its original form the model attributed the formation of the conduction band to overlapping tungsten  $5d(t_{2g})$  orbitals. Recently this model has been greatly refined and generalized.<sup>30,31</sup> In particular, the role which the oxygen orbitals might play in band formation has been examined.<sup>32</sup> It is possible that direct evidence for such an admixture could be obtained from the <sup>17</sup>O NMR in these compounds.

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<sup>30</sup> A. Ferretti, D. B. Rogers, and J. B. Goodenough, *J. Phys. Chem. Solids* **26**, 2007 (1965).

<sup>31</sup> J. B. Goodenough, *J. Appl. Phys.* **37**, 1415 (1966).

<sup>32</sup> It should be noted that the possibility of oxygen  $p_x$  admixtures in the conduction band was first pointed out by Sienko, Ref. 2.

## Lattice Vibrations in Aluminum and the Temperature Dependence of X-Ray Bragg Intensities\*

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x-ray intensity data have been obtained from aluminum single crystals at temperature intervals that were small enough to allow determination of  $d(\ln I)/dT$  in the 100–300°K temperature range. From these measurements the temperature dependence of  $dM/dT$  (or  $M'$ ), the temperature derivative of the Debye-Waller factor  $M$  was determined. These derivatives are related in a straightforward way to the frequency distribution  $g(\nu)$  and hence to an equivalent characteristic temperature  $\Theta_{M'}$ . Comparisons of experimental results with calculations based on actual approximate frequency distributions for aluminum indicate that the sensitivity of  $\Theta_{M'}$  to the shape of the frequency distribution can be experimentally significant. These experimental results for  $\Theta_{M'}$  are in very good agreement with calculations based on a frequency distribution derived by means of an 8-neighbor Born-von Kármán force model from a previously reported analysis of neutron inelastic scattering data. Calculations using a simple one-neighbor force model based only on elastic constants were inadequate. In the 100–300°K range the entire temperature dependence of the experimental  $\Theta_{M'}$  can be accounted for by anharmonicity associated with thermal expansion. The experimental and analytical techniques used make possible the determination, at a given temperature, of a relatively accurate and unambiguous value for  $\Theta_{M'}$ . The determination does not depend on  $\Theta_{M'}$  values at other temperatures.

### INTRODUCTION

IN most experimental investigations of the temperature dependences of x-ray Bragg intensities for materials with simple crystal structures, ratios of intensities measured at relatively widely separated temperatures (50–500°K) have been analyzed within the

framework of the Debye-Waller theory to yield values for the Debye-characteristic temperature  $\Theta_M$ . The measurement of such a ratio, however, determines only the difference  $\Delta M$  of the Debye-Waller factors  $M$  appropriate to each end of the temperature interval. Because  $\Theta_M$  itself generally varies with temperature, the interpretation of these differences can be ambiguous<sup>1</sup> unless either  $\Theta_M$  at some reference temperature or the shape of the desired  $\Theta_M$ -vs-temperature curve is known. Such information is rarely (if ever) available with sufficient accuracy, especially for the low-tempera-

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<sup>1</sup> F. H. Herbstein, *Advan. Phys.* **10**, 313 (1961).